ORGANO-MERCURI ESTERS AS A CANDIDATE SYNTHETIC ROUTE FOR INSERTION OF ENERGETIC GROUPINGS

Final Report ONR Contract Nonr 4519(00)

by

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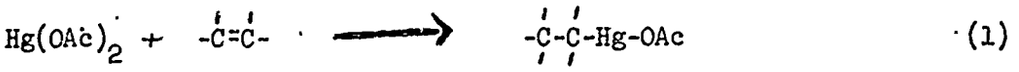
NR 093-044/8-1-66
ONR:630:IAD

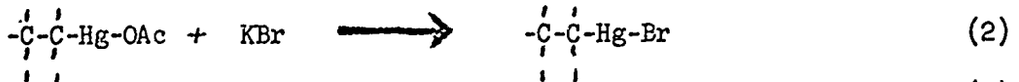
Introduction:

Mercuric esters are readily alkylated by reaction with olefines:

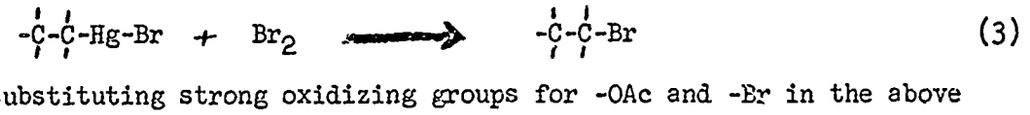


(1)

The resulting alkylmercuri-compounds can undergo further displacement reactions involving the mercury atom:

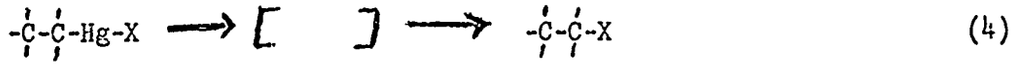


(2)



(3)

By substituting strong oxidizing groups for -OAc and -Br in the above sequence of reactions, it might be possible to effect their ultimate attachment directly to the alkyl carbon atom:



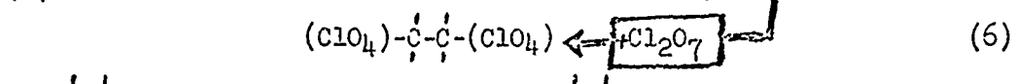
(4)

Of particular interest are compounds in which the "X" substituent of equation (4) is $-ClO_4$ or $-NF_2$.

Conclusions:

Exploration of the reaction schemes:

(5)



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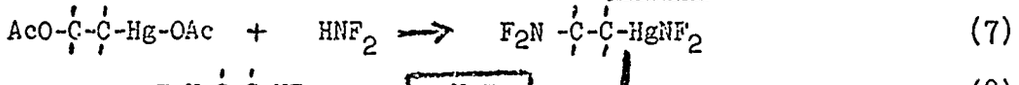

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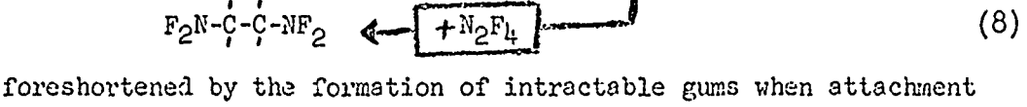

(8)

was foreshortened by the formation of intractable gums when attachment of the energetic grouping to the mercury atom was essayed. Some presumptive evidence for the formation of $-C-(ClO_4)$ and $-C-NF_2$ was developed, and a number of intermediates were synthesized.

Details:

a) Prefatory

The acetoxymercuration reaction of equation (1) above is effective on a wide variety of olefinic compounds[1,2,3], and in fact has been advocated as an analytical method[4] because the reaction is quantitative in so many instances. Additional versatility stems from companionate reactivity of the polar reaction media employed. In reaction (1) above, for example, the use of alcohols:

$$Hg(OAc)_2 + -\dot{C}=\dot{C}- + ROH \longrightarrow RO-\dot{C}-\dot{C}-Hg-OAc \qquad (9)$$

while water or glacial acetic acid produce $HO-\dot{C}-\dot{C}-Hg-OAc$ and $AcO-\dot{C}-\dot{C}-Hg-OAc$ respectively. Moreover, other types of mercuric esters will react, e.g.:

$$HgF_2 + F_2C = CFCl \longrightarrow F_3C-C(Hg-F)FCl \qquad (10)$$

and the additions of $HgCl_2$ have been widely studied[5].

With respect to energetic groupings, the additions of $Hg(NO_3)_2$[6], $Hg[C(NO_2)_3]_2$[7], and $Hg(ClO_4)_2$[8,9] have all been investigated.

Little has been done to examine the metathetical possibilities of reaction (2), however. For example:

$$-\dot{C}-\dot{C}-Hg-OAc + K\,ClO_4 \longrightarrow -\dot{C}-\dot{C}-Hg-ClO_4 \qquad (11)$$

$$-\dot{C}-\dot{C}-Hg-Br + AgClO_4 \longrightarrow -\dot{C}-\dot{C}-Hg-ClO_4 \qquad (12)$$

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1. J. Romeyn, G. Wright J. Am. Chem. Soc. 69 697-701 (1947)
2. J. R. Johnson, W. H. Jobling, G. W. Bodamer, ibid. 63 131-5 (1941)
3. K. Kato Nippon Kagaku Zasshi 81 829 (1960) (CA 56 493a (1962))
4. J. B. Johnson, J. P. Fletcher Analytical Chem. 31 #9 1563-4 (1959)
5. J. Chatt Chem. Rev. 48 7-44 (1951)
6. I. L. Knunyants, E. Ya. Pervova, V. V. Tyvleneva Invest. Akad. Navk S.S.S.R. Otdel. Khim. Navk 1961 88-93 (CA55197758)
7. V.A. Tartakovskii, S.S. Novikev, I.T. Godovikove, ibid. 1961 1042-8 (CA55270250)
8. E.R. Allen, J. Cartlidge, M.M. Taylor, C.F.H. Tipper J.Phys.Chem. 63 1437-9 (1959)
9. P. Brandt. O. Plum Acta Chem. Scand. 7 97 (1953)

and essentially nothing parallel to reaction (3), e.g.:

$$-\dot{C}-\dot{C}-Hg-NF_2 + N_2F_4 \longrightarrow -\dot{C}-\dot{C}-NF_2 \qquad (13)$$

b) Perchlorates

Allen et al[8] have shown both ethylene and propylene to react rapidly with aqueous solutions of $Hg(ClO_4)_2$. Although the adduct could not be isolated, it was presumed (on analogy with previous additions of $HgCl_2$) to be β-hydroxyethyl perchlorate from the reactions:

$$Hg(ClO_4)_2 + H_2O \longrightarrow HO-Hg(ClO_4) \qquad (14)$$

$$HO-Hg(ClO_4) + H_2C=CH_2 \longrightarrow HO-CH_2CH_2-Hg(ClO_4) \qquad (15)$$

or possibly from the equivalent scheme:

$$Hg(ClO_4)_2 + H_2C=CH_2 \longrightarrow -CH_2-CH_2-Hg(ClO_4) \qquad (16)$$

$$HO-CH_2-CH_2-Hg(ClO_4) \xleftarrow{+H_2O} \qquad (16\text{-a})$$

The reaction velocity was uncontrollably high, until "moderated" by pyridine.

We have investigated various steps in the proposed reaction sequence of equations (5) and (6) above. We have found that the reaction velocity in (5) can be readily controlled, without additives, by incremental addition of the olefine to an agitated aqueous solution of $Hg(ClO_4)_2$, the latter being linked with a liquid expansion reservoir to gauge and control the rate of gas absorption. A typical experiment follows:

MVK I-16

A 10-molar $Hg(ClO_4)_2$ solution is prepared in a 500 ml. Erlenmeyer flask containing a Teflon-coated magnetic stirrer bar, 1" in length. To 143.0 gms. of stirred 70% aq. $HClO_4$ (1 mole) are added 108.3 gms. (0.5 mole) of red HgO in 5 increments over the course of an hour, each increment reacting to form a clear brownish solution before more of the initially-insoluble HgO is added. The reaction temperature rises from an initial 25°C. to ca 40°C. which is barely sufficient to prevent crystallization of the product (probably the tetrahydrate, according to Peschanski[9-a]).

MVK I-25

The hot 10-molar solution from above was diluted with distilled water to 2-molar and 150 ml. of the latter were placed in a 250-ml. suction flask. A 25 ml. pipette served as a liquid surge reservoir by projecting through the Neopreme stopper and to the flask's bottom. The stopper was bored at an angle to maintain the pipette parallel to the sloping wall of the flask and out of conflict with the magnetic stirrer bar. The side-arm of the flask was connected to a tank of ethylene by "Tygon" tubing and the usual sequence of reducing and needle valves on the tank. Ethylene was admitted to the flask until its pressure forced $Hg(ClO_4)_2$ solution up to the calibration line of the pipette. Gas was shut off and reaction at room temperature was observed as the liquid level in the pipette declined. The latter rate varied widely depending upon the vigor of the agitation. Approximately the theoretical amount of C_2H_4 reacted in 45 minutes at which point gas "absorption" ceased. The reaction rate is steady until about 50% of the theoretical amount of gas had reacted at which time a pronounced increase in the rate was noted. The final clear solution did not give any evidence of decomposition, e.g. gas evolution, after a week's storage at room temperature.

Additional experiments showed the reaction to proceed in solutions of $Hg(ClO_4)_2$ ranging in concentration from 0.037 molar up to 10 molar with no observable change in velocity. The more concentrated solutions (i.e. $\geq 8M$) did require warming to repress crystallization of the starting material, but otherwise the reactions all proceeded with alacrity at room temperature. The reaction time could readily be shortened by more vigorous agitation and/or pressurization - a gas burette with a Hg-filled leveling bulb being used in these latter experiments to apply a few cm. "head" to the reaction zone. The increased reaction rate encountered part-way through the reaction was checked by repetitive experiments and was actually noted in many other instances, particularly in the more concentrated solutions where depletion of the limited amount of water available, via reactions (11) and (12), or (13), might alter the polarity of the reaction zone.

Parallel experiments with butene-1 (MVK I-27) and aqueous $Hg(ClO_4)_2$ discovered a marked decrease in reaction rate @ 4.0 molar, and gas

absorption virtually ceased at 5.0 molar. By pressurizing with ca. 10 cm. "head" of mercury in a gas burette, reaction could be effected up to 10 molar, again with 8 molar being a pragmatic limit because of crystallization in the starting solutions.

Evaporation of the above aqueous reaction mixtures failed to yield an identifiable product in all cases, whether the water was removed by evacuation at 25°C./0.1 mm or by dessication over P_2O_5. The residue was invariably a brown-to-black, non-crystalline mush or gum, possibly the same material noted by Allen and co-workers[8]. Prolonged extraction of the aqueous reaction mixtures with immiscible solvents such as hexane, benzene and diethyl ether failed to separate any organic material. The product of the butene-1 reaction occasionally had a faint ester-like odor, and in general tended to a darker color than that of the ethylene reaction product. Both residues ignited vigorously @ 160-170°C. and decomposed with erratic flashes of light.

Assuming that the hydroxyl group of the above adduct would render dehydration difficult and encourage decomposition, anhydrous $Hg(ClO_4)_2$ was prepared for addition to olefines.

VJK I-22

A batch of 10 molar aqueous $Hg(ClO_4)_2$ (from MVK I-16 above) was suction filtered at room temperature to yield ca. 75 gm. of crystalline mass. Assuming the hydrate to be in equilibrium with the 10 molar mother liquor, the crystals might contain up to about 15 gms. H_2O, and would thus require somewhat less than 42 gms. anhyd. P_2O_5 for complete dessication.

Approximately 50 gm. P_2O_5 were placed on a watch glass in the lower chamber of a vacuum dessicator above which the 75 gm. $Hg(ClO_4)_2$ crystals were located. The dessicator was evacuated to ca. 35 mm. and allowed to stand for 2 days at room temperature. By this time the erstwhile clear crystals had whitened and the P_2O_5 had acquired a heavy coating of phosphoric acid. The $Hg(ClO_4)_2$ crystals were ground in a mortar and quickly restored to the dessicator wherein a fresh P_2O_5 surface had been exposed by scraping off the gummy "crust."

This procedure was repeated twice when no further loss in weight of the white $Hg(ClO_4)_2$ powder could be detected $\pm$ 0.01 gm. This dessicated $Hg(ClO_4)_2$ is extremely deliquescent, insoluble in ligroin, benzene glacial acetic acid, liquid SO_2 and diethyl ether. It is moderately soluble in dimethyl formamide (DMF) and in tetrahydrofuran (THF), and dissolves slowly in denatured ethanol.

The direct, undiluted reaction of $Hg(ClO_4)_2$ with the olefine was first checked.

VJK I-34

A 100 ml. round bottom flask was first fitted with a stopper containing a drying tube filled with anhydrous $CaCl_2$ and then immersed in a dry ice-and-acetone bath. An excess of butene-1 (40.8 gms., ca. 0.725 moles) was condensed therein on 20 gm. (0.05 mole) of dessicated $Hg(ClO_4)_2$ and the flask was re-fitted with a dry-ice condenser. The reaction mixture was agitated by a magnetic stirrer bar and allowed to warm up to reflux temperature. The powdered $Hg(ClO_4)_2$ did not dissolve but soon formed an opaque white fluid phase in the bottom of the flask which gradually turned reddish-brown in the course of 35 minutes reaction.

The reaction was then halted, the clear supernatant layer was separated and allowed to evaporate at room temperature, leaving only a trace of oily material with a sharp odor. The residual gummy paste had a distinct ester odor and its weight had increased by somewhat greater than 1.0 gm. over that of the starting $Hg(ClO_4)_2$ - theory for 1:1 adduct = 2.3 gms.

The residue was only sl. soluble in acetone, methylene chloride, ligroin and DMF (deep red

coloration). It turned yellow in water and gray-black in dilute aqueous NaOH (5% soln.). Upon standing 3 days in a closed container, it developed no pressure, indicative of further decomposition, and no odor of butene could be detected.

A differential scan of a solution of the gummy residue in DMF vs. DMF alone (Perkin-Elmer Model 337 KBr cell windows, 0.025 mm. path. "Normal" slit width, "Fast" scan) showed a broad peak @ 3140 cm-1 (20% absorbance), a sharp doublet @ 1950 and 1860 respectively (20-30% absorbance) and the major peak @ 1170 (80% absorbance) and a modest one (20% absorbance) @ 450 cm-1. IR spectra of the dessicated $Hg(ClO_4)_2$ in both dilute DMF solution and in Nujol "mull", show the major absorption peak almost precisely @ 1100 cm-1 and none of the other peaks encountered with the above adduct.

Despite the unsatisfactory form of the above reaction product, the IR absorption spectrum displays a number of the salient features characteristic of several perchlorate salts[10], particularly their major peak @ ca. 1100 cm-1. The small displacement of this peak in the above reaction product is possibly a significant comment on the similarity in state of ionic perchlorates such as $KClO_4$ and the covalent modifications such as the R-Hg-(ClO_4) which should be present in the above adduct. Moreover, the ability of the perchlorate grouping to dominate its environment is well-known as illustrated by the marked conductivities of numerous metal perchlorates in a variety of organic solvents.[11,12,13]

Attempts at better control of the $Hg(ClO_4)$ addition reaction included the use of several diluents:

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10. F. A. Miller, C. H. Wilkins Analytical Chem. 24 1283 (1952)
11. Mollard, H. E. & Smith, G. F. J. Am. Chem. Soc. 45 286 (1923)
12. Griffiths, V.S. & Pearce, M. L. J. Chem. Soc. 1927 p. 3245
13. Luder, M.F., Kraus, P. B., Kraus, C. A. & Fuoss, R. M. J. Am. Chem. Soc. 58 255 (1936)

a) Liquid SO_2 - even a several-fold excess failed to dissolve the $Hg(ClO_4)_2$ and a multi-phase, poorly defined reaction product resulted.

b) DMF - slowly dissolved the $Hg(ClO_4)_2$ with considerable evolution of heat, but little discoloration. Within 24 hours a deposition of metallic mercury is visible.

c) Ethanol will dissolve $Hg(ClO_4)_2$ (e.g. 20 gms./200 alcohol - VJK I-46) and this mixture absorbs butene-1 very slowly. Even a moderate shock detonates the reaction mixture and these experiments were discontinued.

d) THF will dissolve a limited amount of $Hg(ClO_4)_2$ with some evolution of heat.

VJK I-41

The procedure and apparatus were similar to those employed above in MVK I-16, but a 125 ml. suction flask and a 50 ml. pipette were used. The tip of the latter was broken to expose the maximum bore of the lower leg of the pipette and avert plugging by the initial slurry of reactant.

Twenty gms. $Hg(ClO_4)_2$ and 52.5 gm. THF were slurried and agitated during the addition of butene-1 at 25°C. Discoloration occurred almost immediately and slowly developed into a clear brown color as the reaction progressed and the remaining $Hg(ClO_4)_2$ dissolved. At the end of ca. 48 hours, the mixture had absorbed $< 50\%$ of theory and the rate of addition had decreased almost to zero. After standing overnite @ 15°C., the red-brown liquid deposited a film of gray paste on the walls of the flask. The liquid was suction-filtered and allowed to evaporate at room temperature. As solvent evaporated, the red-brown residue became more viscous and continued to deposit a layer of gray powder on the bottom of the flask. When evaporation of solvent ceased, the resulting deep-red gum was found to be soluble in acetone, methanol, conc. H_2SO_4 and conc. HCl; insoluble in ligroin, xylene, methylene chloride and aN NaOH. IR scan showed the same general pattern of absorbance as in the adduct from VJK I-34 above. No solid could be recrystallized from acetone or methanol solutions of the red gummy residue.

On a hot plate the red gum ignites with great vigor @ ca. 175°C. and burns with a crackling noise and radiating luminous "sparks". (Dessicated $Hg(ClO_4)_2$ shows none of these effects at the same temperature.)

The above reaction probably deserves further scrutiny, despite evidence of some continuing decomposition to a gray powder. If the $Hg(ClO_4)_2$ reactant is indeed completely anhydrous, either its components have added on both sides of the olefinic link, i.e. (ClO_4)-C-C-$Hg(ClO_4)$, or the THF ring has been ruptured to provide an adductive moiety, i.e. (THF res.) -C-C-$Hg(ClO_4)$.

Meanwhile, the further groundwork for reaction (5) was established by investigation of the addition of anhydrous $HClO_4$ to olefines. Contrary to the experience of others[14], we have encountered no difficulty in controlling this reaction when diluents are employed. Actually, pure anhydrous $HClO_4$ can be mixed directly with liquid butene-1 although exceedingly vigorous agitation and heat exchange are necessary to control the violent reaction and avert detonation. The reaction in solvents is uneventful and more convenient.

VJK I-71

Anhydrous perchloric acid is made essentially by the method of Smith[15]. The apparatus is a 100 ml. round-bottom flask equipped with a thermometer well and surmounted by a very short distillation "head" whose side-arm leads directly to an ice-cooled receiver equipped with a vacuum connection. All connections are ground glass, lubricated with fluoro-carbon"grease". Eleven ml. of commercial 72% $HClO_4$ are placed in the flask and cooled to 10°C. after which a total of 43 ml. of 20% fuming H_2SO_4 are added incrementally in the course of 20 minutes so as to avoid any significant rise in temperature. The apparatus is then evacuated to 0.5 mm. and the flask warmed gradually (e.g. 30 minutes) to ca. 35°C. at which point clear, colorless $HClO_4$ begins to collect in the receiver. The reaction temperature is slowly raised to about 40-45°C. at which point vigorous

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14. Tauber, S. J. & Eastham, A. M. J. Am. Chem. Soc. 82 4888-91 (1960)
15. Smith, G. F. J. Am. Chem. Soc. 72 184-6 (1953)

bubbling is observed in the flask and distillation continues, the thermometer in the condensing vapor overhead reading 20°C. uncorrected. In the next 45 minutes, the pot temperature is slowly raised to 65° and gradually distillation ceases, yielding 9.6 gms. of clear, very pale green $HClO_4$ in the receiver.

VJK I-90

Thirteen gms. (o.13 moles) of anhydrous $HClO_4$, made as above, are admixed with 80 ml. benzene in a 125 ml. suction flask equipped with stopper and a canted 50 ml. pipette as previously described. Ethylene gas was admitted by a gas burette to the side-arm of the reaction flask. In the course of 2 hours, the stirred solution absorbed ca. twice the theoretical volume of olefine. The reaction mixture was dark red-brown in color and had deposited traces of brown gum on the walls of the flask. The solution was washed to neutrality with saturated Na_2CO_3 solution and dried 16 hours over $CaCl_2$.

The differential IR scan against pure benzene showed a strong triplet peak in the absorbance curve @ 2750-2900 cm-1 (ethyl?), a strong single peak @ 1475 (ethyl?) as well as a strong doublet @ 1235-1260 cm-1.

Attempts to distill out pure ethyl perchlorate invariably led to severe darkening of the residual solution in the still pot and its ultimate detonation. The benzene solution ignites when heated to 200°C. and burns vigorously.

The IR absorbance @ 1235-1260 cm-1 could be attributed to covalently-bound perchlorate; at least it is at a higher wave number than the inorganic perchlorate (~1100 cm-1) much as the covalent sulfate, sulfonate, phosphate and nitrate are above their ionic counterparts.

The absorption of more than the stoichimetric amount of ethylene in the above reaction is not completely unexpected in view of previous work on butene-2, but no satisfactory explanation can be offered as yet. The effect of the solvent can be pronounced - at least the same reaction in $CHCl_3$ absorbs ca. 50% of the theoretical amount of ethylene (VJK I-98-A) but gives very strong absorbance in a doublet @ 1260 and 1210. It is noteworthy that after removal of benzene from the reaction mixture the residue ignites

@ 200°C. with an audible "pop" and also explodes when struck with a hammer on an iron anvil. The benzene solution of the reaction mixture from above was inert to a comparable hammer blow.

Butene-1 undergoes a comparable reaction with a $CHCl_3$ solution of $HClO_4$, with a total gas absorption of ca. 50% of theory (VJK I-94-A). However, severe darkening of the reaction mixture is encountered and indeed some light flashes with ejection of the flask stopper were noted if the reaction rate wasn't moderated by minimizing the pressure "head" from the leveling bulb of the gas burette. The IR spectra is grossly similar to that of the ethylene adduct above in displaying a strong peak @ 1210 cm^{-} and "alkyl" type absorbance in the 2600-2900 range.

Moreover, the latter spectra strongly resembled those of authentic samples of butyl perchlorate made by metathesis of butyl iodide with silver perchlorate in benzene solution. The spectra of the adduct compared more closely with that of the sec-butyl perchlorate (from 2-iodobutane). The latter ester attacks the cork stopper upon standing 2-4 weeks in benzene, whereas the n-butyl perchlorate seems unreactive.

VJK I-60

Hills preferred method[16]:

$$Ag_2O + HClO_4 \longrightarrow AgClO_4 \qquad (17)$$

gave erratic results, possibly because of the variable strength of the commercial $HClO_4$. In any event, the alternate route:

$$AgNO_3 + HClO_4 \longrightarrow AgClO_4 \qquad (18)$$

was found to produce benzene-soluble material exclusively.

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16. Hill, A. E. J. Am. Chem. Soc. 43 257 (1921)

Typically, 5 gm. $AgNO_3$ and 20 gm. of commercial 70% $HClO_4$ were heated in a hood for 2 hours @ 110°C. until the fumes had disappeared. Upon cooling, white crystals formed in the residue and they could be easily dissolved in hot benzene, filtered and recrystallized.

Metathesis with the alkyl iodides followed Redies and Iredale[17].

Repeated, unsuccessful attempts were made to add ethylene and butene-1 to a mixture of $Hg(ClO_4)_2$ and $HClO_4$. The insolubility of the $Hg(ClO_4)_2$ produced some interfacial reaction to judge by the discoloration of that boundary, but a purple-brown paste resulted with considerable supernatant liquid. The latter was presumably unreacted $HClO_4$ since it reacted vigorously with Na_2CO_3 solution. IR scan of a Nujol mull of the above-mentioned paste did not display any concrete evidence of the formation of the desired compound, (ClO_4)-C-C-$Hg(ClO_4)$.

Attempts to employ THF as a reaction solvent were adjudged too dangerous in view of the violent eruption induced by one drop (est. 1/30 ml.) of pure $HClO_4$ in a large excess (25 ml.) of THF.

c) Fluoramines

Prototype reactions were investigated for the proposed sequence:

$$\text{C=C} + Hg(OAc)_2 + HOAc \longrightarrow ACO\text{-C-C-Hg-OAc} \qquad (19)$$

$$FN\text{-C-C-Hg-}NF_2 \xleftarrow{[HNF_2]} \qquad (7)$$

$$F_2N\text{-C-C-}NF_2 \xleftarrow{[+N_2F_4]} \qquad (8)$$

The addition of mercuric acetate to ethylene in the presence of methyl or ethyl alcohols or of glacial acetic acid proceeds readily.

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17. Redies, L. P. & Iredale, T. J. Phys. Chem. 48 224 (1944)

MWK I-3,5

Forty grams (0.125 mole) of commercial anhydrous $Hg(OAc)_2$ were suspended in 225 ml. absolute ethanol (ca. 3.85 moles) by agitation of a 1-inch magnetic stirrer bar within a 500 ml. suction filter flask equipped with a stopper and a canted 200 ml. pipette as before. The tip of the pipette had been removed to permit free passage of the slurry. The amount of ethanol is selected to fill the pipette and still leave enough liquid in the flask below to cover the lower end of the pipette. Heat may be supplied to increase the solubility of the $Hg(OAc)_2$ in the ethanol somewhat, but the resulting adduct dissolves in the ethanol as formed and the reaction proceeds briskly at room temperature if adequate mixing is provided.

The theoretical amount of ethylene is absorbed within 35 minutes at which point the reaction ceases, leaving a clear solution with a trace of grey powder. The latter is removed by suction-filtration and ca. 85% of the alcohol-acetic acid mixture is removed by distillation @ atmospheric pressure. Upon cooling, the distillation residue solidifies and this can be hastened by refrigeration. The product is too soluble in ethanol for recrystallization and hence it is recrystallized twice from 30-60° ligroin (hot extraction) to yield a sharp-melting white solid m. pt. 37-8°C. uncorr., presumably $Et\text{-}O\text{-}CH_2\text{-}CH_2\text{-}HgOAc$.

VJK I-123

In the above apparatus, 40 gms. (0.125 mole) of $Hg(OAc)_2$ were suspended, with stirring, in 120 gms. glacial HOAc. The reaction mixture absorbs ethylene slowly in comparison with the preceding reaction in alcohol, requiring about 3.5 hours even when heated to 60°C. The clear solution is then filtered to remove traces of flocculent precipitate and vacuum distilled @ ca. 10 mm. to remove ca. 85% of the acetic acid. The residual white solid cake is insoluble in hot ligroin but can be recrystallized from $CHCl_3$ to yield a white crystalline solid melting @ 98-9° uncorr., presumably $ACO\text{-}CH_2\text{-}CH_2\text{-}HgOAc$.

The conversion of the above esters to the corresponding fluoramines (reaction (7) above) should proceed via the reagent HNF_2[18] whose displacement

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18. This reagent was supplied by Aerojet-General Corp., in the form of N,N-difluorourea solution, through the kindness of Dr. K. Baum.

of other "active" ester groups is well-documented.

VJK I-153

In a 250 ml. suction filter flask, 13.28 gms. (0.04 mole) of EtO-CH_2-CH_2-HgOAc from MWK I-3,5 above were dissolved in 40 ml. CH_2Cl_2. The solution was agitated gently and 38.4 ml. of Aerojet-General Corp. solution of N.N-difluorourea (@0.1 gm./ml. + 3.84 gms. + 0.04 mole) were added. To this solution, 4.4 ml. of 95-98% H_2SO_4 were added dropwise producing an immediate opacity in the reaction mixture which settled out within 5 minutes as a brown gummy fluid on the bottom of the flask. Agitation was continued for 30 minutes with no visible change in the mixture. The gum was washed with 3 fresh 50 ml. volumes of CH_2Cl_2 without visibly altering its appearance or viscosity. It was insoluble in methanol, ethanol, diethyl ether, chloroform, xylene and DMF and THF.

No IR scan could be made because of the dark color of the gum, even in thin films coated directly on K Br "windows" of an IR absorption cell (The film seemed to absorb, or react, with the window and form a completely opaque layer which could be removed only by very vigorous scrubbing). Attempts to mull the gum in mineral oil failed because the oil did not wet the gum and no suspension thereof could be effected.

The formation of an insoluble, intractable gum in the above reaction was disappointing and the B-acetoxymercuriethyl acetate of VJK I-123 above formed a similar gum. The reaction with N_2F_4 was checked.

VJK I-153

The gum in the above (VJK I-153) suction flask was covered with ca. 250 ml. of a 3/1, by volume, mixture of CCl_2F-$CClF_2$ and $CHCl_3$, and this mixture was saturated by ca. 800 ml. gaseous N_2F_4[19]. The mixture was stirred 16 hours at room temperature without appreciable discoloration of the supernatant liquid and only a slight darkening of the gum in the bottom of the flask.

The supernatant liquid was decanted, washed with 5% $NaCO_3$ solution, dried 12 hours over $CaCl_2$ and distilled.

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19. Furnished by the U. S. Naval Ordinance Station at Indian Head, Md., through [illegible] and by Dr. Roquiston thereof and Mr. R. K. Renton of the Office of Naval Research.

All of the material boiled below 65°C. and IR scan showed only the absorbance expected for the two solvents.

The gummy residue appeared little changed from the starting material. It was insoluble in all the organic solvents tried previously, it was too dark for an IR absorbance scan and it could not be mulled in mineral oil or chlorinated aromatics.

The lability of the acetory group in the starting material above, i.e. Et-O-Et-Hg-OAc was checked by treatment of concentrated alcoholic solution of KI. The customary voluminous yellow-green precipitate of the iodomercuri-compound developed immediately and recrystallization from ethanol yielded a compound melting 46-48°C., uncorrected.

The sensitivity of the iodine substituent in this compound to N_2F_4 was then checked.

VJK I-130

Seventeen grams (0.044 moles) of the iodomercuri compound from above (presumably EtOEtHgI) form a saturated solution in a mixture of 120 ml. "TC-solvent" (an azeotrope of $CHCl_3$ and CCl_2F-$CClF_2$) and 60 ml. $CHCl_3$[20].

This mixture is treated with N_2F_4 in the same gas absorption apparatus as used in the perchlorate experiments above. The temperature is kept below 10°C. to ensure rapid absorption of the N_2F_4. Even if some of the starting material is undissolved at the outset it soon disappears to form a clear yellow-brown solution from which a bright red powder later begins to separate, e.g. after solution of ca. 500 ml. gaseous N_2F_4, and deposit on the walls of the apparatus.

Absorption is complete within 3-4 hours and varies somewhat in total amount but never exceeds of 2 moles N_2F_4/mole iodomercuri compound (VJK I-149).

The red solid is filtered and dried. It melts @ >200°C. with decomposition to a yellow-brown solid. The filtrate is washed with 5% aqueous Na_2CO_3, dried

20. The freon-type solvents would be preferable for their inertness to N_2F_4, but they have little solvent power for these organo-mercury compounds. Hence, the minimal volume of $CHCl_3$ is added to achieve solubility.

16 hours over $CaCl_2$ and distilled to remove 85-90% of the solvents. The residual liquid, when chilled, yields a pale yellow-green solid presumably the starting iodo compound since a mixed m. pt. shows no depression.

The mother liquor shows a moderate (e.g. 25%) IR absorbance peak - 2900 cm-1 - and strong, i.e. + 85% absorbance peaks @ 1290, 1150, 1110, a cluster at 940-905 and doublets @ 870-850 and @ 685-700 cm-1. The cluster @ 900 cm-1 may characterize the N-F assymetric stretching mode and indeed the spectra shares a number of the absorbance peaks reported by C. Coburn[21] for gaseous $E+OE+NF_2$.

Vacuum distillation of this clear, pale yellow residue yields only a trace of liquid boiling in the expected range of 38-42°/27 mm. accompanied by extensive decomposition in both the liquid and vapor phases of the still pot.

Larger batches of starting material failed to yield significant increases in this fraction, nor did major alterations in the solvent ratio, amount of $CHCl_3$ present, reaction time, and purity of starting material improve the process. If the B-fluoraminoethyl ethyl ether is truly present, it must be only as a very minor by-product of a complex process.

NOTE: These organo-mercurials share the irritant-vessicant action of many others of their class. Extreme care should be exercised to avoid contact with the skin. Safe handling should involve protective cream, washable cotton mitts, and heavy duty latex rubber gloves.

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21. Rohm & Haas Co., Huntsville, Alabama - private communication.